PRINCIPLES OF POLYMERIZATION

Third Edition

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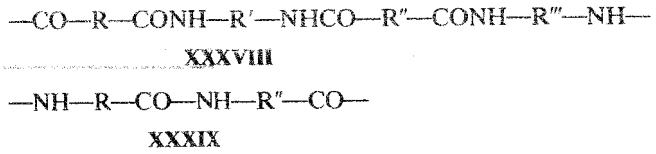
2-13a Types of Copolymers

Further variation is possible in the polymer structure and properties by using mixtures of the appropriate reactants such that the polymer chain can have different R and R′ groups. Thus polyamide structures of types **XXXVIII** and **XXXIX** are possible variations on structures



—CO—R—CONH—R′—NHCO—R″—CONH—R‴—NH—

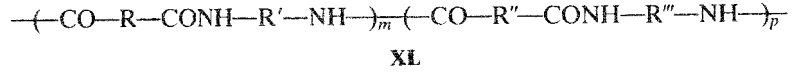
XXXVIII

—NH—R—CO—NH—R″—CO—

XXXIX

XXXVI and **XXXVII**, respectively. A polymer such as **XXXVIII** or **XXXIX** has two different repeat units and is referred to as a *copolymer*; the process by which it is synthesized is referred to as *copolymerization*. Polymers with structures **XXXVI** and **XXXVII**, each containing a single repeat unit, may be referred to as *homopolymers* to distinguish them from copolymers.

Different types of copolymers are possible with regard to sequencing of the two repeating units relative to each other. Thus a copolymer with an overall composition indicated by **XXXVIII** could have the *alternating copolymer* structure shown in **XXXVIII** in which the R, R′, R″, and R‴ groups alternate in that order over and over again along the polymer chain, or the *block copolymer* structure **XL** in which



—(—CO—R—CONH—R′—NH—)$_m$—(—CO—R″—CONH—R‴—NH—)$_p$—

XL

blocks of one type of homopolymer structure are attached to blocks of another type of homopolymer structure, or the *statistical copolymer* structure in which there is an irregular (statistical) distribution of R and R″ groups as well as R′ and R‴ groups along the copolymer chain. Similarly, one can have alternating, block, and statistical copolymers for the overall composition **XXXIX**.

For the statistical copolymer the distribution may follow different statistical laws, such as Bernoullian (zero-order Markov), first- or second-order Markov, depending on the specific reactants and the method of synthesis. This is discussed further in Secs. 6-2 and 6-5. Many statistical copolymers are produced via Bernoullian processes wherein the various groups are randomly distributed along the copolymer chain; such copolymers are *random copolymers*. The terminology used in this book is that recommended by IUPAC [Ring et al., 1985]. However, most literature references use the term *random copolymer* independent of the type of statistical distribution (which seldom is known).

The alternating and statistical copolymer structures can be symbolized as

~~~ABABABABABABABABABABABAB~~~

Alternating copolymer

~~~AABABBBABAABAAABBABBBAAB~~~

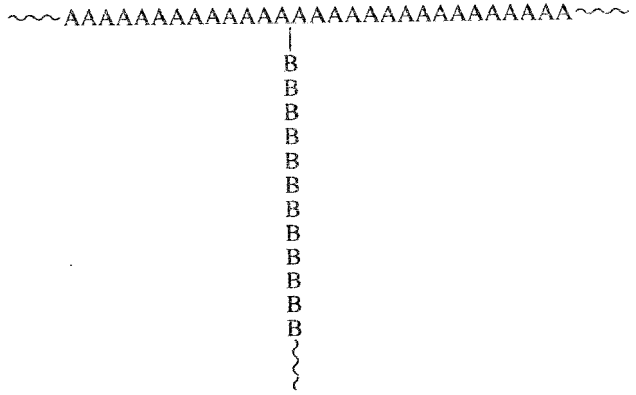
Statistical copolymer

where A and B represent two different repeating units. Different block copolymers are distinguished by the number of blocks per molecule, for example,

A_mB_p	$A_mB_pA_m$	$A_mB_pA_mB_p$	$(A_mB_p)_n$
Diblock	Triblock	Tetrablock	Multiblock

which are referred to as AB diblock, ABA triblock, ABAB tetrablock, and AB multiblock copolymers, respectively. For the various block copolymers the values of m and p as well as n are average values; thus, there is a distribution of block lengths and number of blocks along the copolymer chain. There is considerable structural versatility possible for statistical and block copolymers in terms of the relative amounts of A and B in a copolymer. For block copolymers there is the additional variation possible in the number of blocks of A and B and their block lengths (values of m and p).

Alternating, statistical, and random copolymers are named by following the prefix "poly" with the names of the two repeating units. The specific type of copolymer is noted by inserting *-alt-*, *-stat-*, or *-ran-* in between the names of the two repeating units; *-co-* is used when the type of copolymer is not specified, i.e., poly(A-*co*-B), poly(A-*alt*-B), poly(A-*stat*-B), poly(A-*ran*-B). Block copolymers are named by inserting *-block-* in between the names of the homopolymers corresponding to each of the blocks. The di-, tri-, tetra-, and multiblock copolymers are named as polyA-*block*-polyB, polyA-*block*-polyB-*block*-polyA, polyA-*block*-polyB-*block*-polyA-*block*-polyB, and poly(polyA-*block*-polyB), respectively. Adoption in the literature of some of these IUPAC recommendations for naming copolymers has been slow.



Graft copolymer

A fourth type of copolymer is the *graft copolymer* in which one or more blocks of homopolymer B are grafted as branches onto a main chain of homopolymer A. Graft copolymers are named by inserting *-graft-* in between the names of the corresponding homopolymers with the main chain being named first (e.g., polyA-*graft*-polyB). Graft copolymers are relatively unimportant for step polymerizations because of difficulties in synthesis. Graft copolymers are considered further in Sec. 9-8.

The discussion to this point has involved copolymers in which both repeating units have the same functional group. A second category of copolymer involves different